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ON THE DISSOCIATION OF THE TRIARYLCARBINOLS

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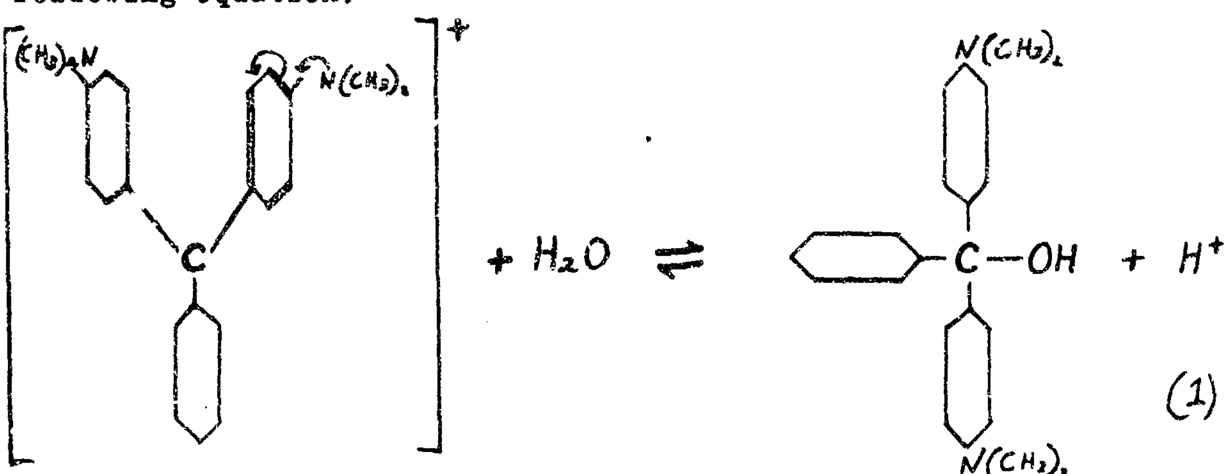
In the 90's of the last century it had already been shown that the basic triphenylmethane dyes, in aqueous solution, undergo hydrolysis {1}. As a result of this hydrolysis a chemical equilibrium is gradually established in the solution, which in the case of malachite green, for instance, may be represented by the following equation:



(1)

From equation (1 M) it follows by quantitative study of the hydrolysis reactions it should be possible for us to determine the dissociation constants of the so-called carbinol bases of the triphenylmethane dyes, that involve a detaching of hydroxyl groups from the methane carbon atoms.

Having produced in chemically pure form the hydriodide and hydrobromide salts of malachite green and of crystal violet, we determined the pH's of their aqueous solutions at temperature 19 ± 1°C. The values found are shown in Table 1.

Table 1

Preparation No.	Name of dye	C (mole/l)	pH	
			Found	Calculated (for 25°C)
1	Hydrobromide of malachite green	$1.48 \cdot 10^{-3}$	4.95	4.86
2	Hydrobromide of malachite green	$1.05 \cdot 10^{-3}$	5.02	4.94
3	Hydrobromide of crystal violet	$7.45 \cdot 10^{-4}$	6.40	6.25
4	Hydriodide of crystal violet	$9.60 \cdot 10^{-4}$	6.35	6.19

Quite recently Goldacre and Phillips [2], on the basis of experimental data obtained from comparing the coloration-intensity of dye solutions at different pH's, calculated, for a number of basic triphenylmethane dyes, characteristics which they called "equilibrium ionization constants", which are in fact the dye hydrolysis-constants. Using these constants, we calculated the pH values which our solutions should possess.

As is seen from Table 1, the experimental and calculated values are extremely close; so too, therefore, the dissociation constants of 4,4'-tetramethyl-diamino-triphenylcarbinol and 4,4',4"-hexamethyl-triamino-triphenylcarbinol, as calculated from the pH's of the dye solutions and as found on the basis of the experimental data obtained by Goldacre and Phillips, are in satisfactory agreement. The dissociation constant found for 4,4'-tetramethyl-diamino-triphenylcarbinol was equal to $9.24 \cdot 10^{-8}$ and that of 4,4',4"-hexamethyl-triamino-triphenylcarbinol equal to $3.76 \cdot 10^{-5}$ (at 19°C).

Continuing with our study of the hydrolysis of the salts from which, when acted upon by alkali, there are formed the "pseudo-bases", we thought it of interest to compare the hydrolysis-constants of these salts in different solvents. To this purpose we determined the hydrolysis-constants of the salts of 4,4'-tetramethyl-diamino-triphenylcarbinol, 4,4'-tetramethyl-diamino-diphenylcarbinol, diantipyryl-phenylcarbinol and 10-methyl-9-phenyl-9-oxy-9,10-dihydroacridine, in aqueous acetone. The hydrolysis-constants were calculated from the pH's of water-acetone solutions containing equimolecular quantities of the carbinol and its salt. Table 2 gives a comparison of the pK's of the above substances in aqueous acetone and in water.

Table 2

Preparation No.	Type of Carbinol	pK In water	pK In aqueous acetone
1	4,4'-tetramethyl-diamino-diphenylcarbinol	5.61*	4.70
2	Diantipyryl-phenylcarbinol	6.56	5.50
3	4,4'-tetramethyl-diamino-triphenylcarbinol	7.07	6.05
4	10-methyl-9-phenyl-9-oxy-9,10-dihydroacridine	9.58	8.55

We should mention that the hydrolysis-constant of malachite green was also calculated on the basis of data obtained in the following experiment. A weighed sample of 4,4'-tetramethyl-

* According to Goldacre Phillip's data [2].

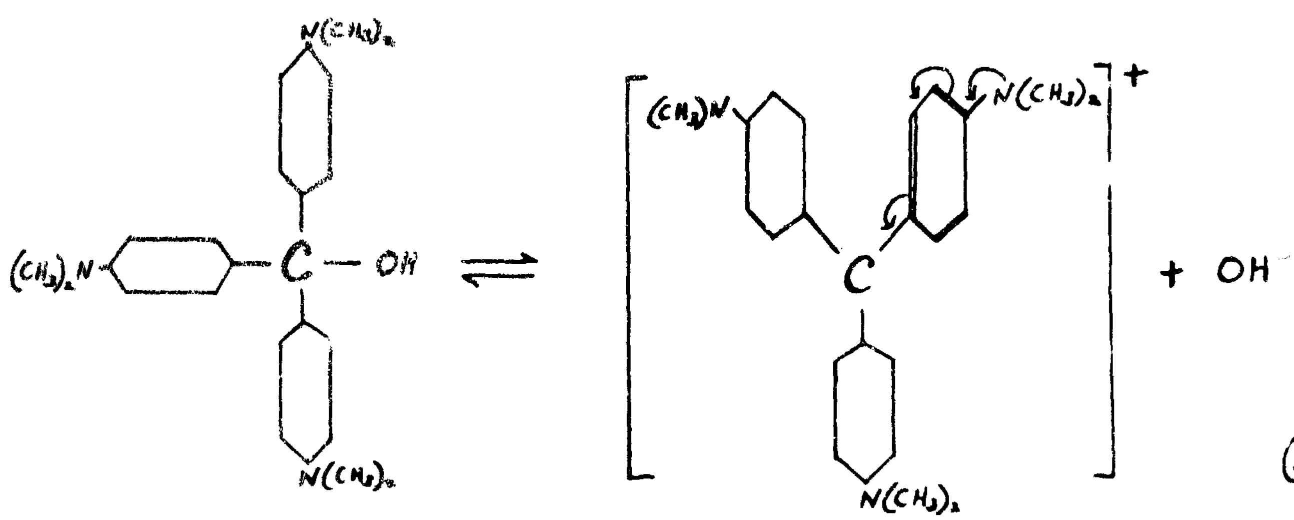
diamino-triphenylcarbinol was dissolved in a precisely measured quantity of aqueous acetone. After this solution had reached equilibrium, the hydrogen ion concentration was determined potentiometrically, and the dye cation concentration pK by colorimetry. pK was * calculated from formula (2) and was found to be 6.06, that is, it was in entirely satisfactory agreement with the value shown in Table 3.

$$pK = pH - \log \frac{[ROH]}{[R^+]} \qquad (2)$$

Since the hydrolysis of the above-mentioned substances constitutes a particular case of acid-base equilibrium, then, as we should expect from Brönsted's Theory (3) when we plot pK in aqueous acetone against pK in water, the points lie quite satisfactorily on a straight line, with the tangent of slope equal to unity.

One might expect that in contrast to aqueous solutions in nitrobenzene, in which it is impossible to have any solvatolysis accompanied by conversion of the dye cation into a compound with the 4-covalent methane carbon atom, the dissociation of the carbinol bases must be very strong. The experiments performed support this idea. Thus, for instance, we prepared nitrobenzene solutions of 4,4'-tetramethyl-diamino-triphenyl-carbinol and of 4,4', 4"-hexamethyl-triamino-triphenylcarbinol, in which the first substance was found to be 70% dissociated and the second 90% dissociated.

Accordingly, our findings in the present experiments fully maintain the thesis that Ganch's so-called "pseudo-bases" are capable of dissociating in various solvents, with the splitting off of a hydroxyl group. This dissociation, in the case of 4,4', 4"-hexamethyl-triamino-triphenylcarbinol for instance, may be represented as in equation (3).



(3)

* Sentence imperfect in text. Two words supplied by translator.

EXPERIMENTAL PART

1. 4,4'-tetramethyl-diamino-triphenylcarbinol

0.1001 g of 4,4'-tetramethyl-diamino-triphenylcarbinol is dissolved in 70 ml of 60% aqueous acetone.

Solution concentration $C = 4.13 \cdot 10^{-3}$ mole/l, solution pH 8.50, temperature 19 ± 1^{o}. The adsorption spectrum of the solution is given in Table 3.

Table 3*

λ mμ	D	λ mμ	D	λ mμ	D
500.0	0.024	600.0	0.490	630.0	0.678
520.0	0.035	620.0	0.652	635.0	0.612
540.0	0.074	622.5	0.679	640.0	0.531
560.0	0.150	625.0	0.690	650.0	0.345
580.0	0.257	627.5	0.686		

The solution thus obtained was acidified with 0.1 n hydrochloric acid solution and diluted 500 times with 60% aqueous acetone. On the following day we took the adsorption spectrum of this dye solution, the pH of which was 4.50 (temperature $19 \pm 1^{o}C$). The concentration C of the dye in the solution was $0.82 \cdot 10^{-5}$ mole/l.

The adsorption spectrum of the solution is shown in Table 4.

Table 4

λ mμ	D	λ mμ	D	λ mμ	D
520	0.008	600	0.212	630	0.365
540	0.027	610	0.295	640	0.285
560	0.070	620	0.366	650	0.178
580	0.131	625	0.375		

2. Determination of pH of Aqueous Solutions of Certain Dyes

A weighed sample of the salt was dissolved in water. The pH's of the solutions in all the experiments were determined by means of a pH-meter with glass and mercurous chloride electrodes at $19 \pm 1^{o}C$. Findings are shown in Table 5.

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* All the spectrophotometric determinations were made with a SF-11 spectrophotometer.

Table 5

Preparation No.	Dissolved Salt	Sample (in g)	Quantity of water (in ml)	pH
1	Hydrobromide of malachite green	0.0607	100	4.95
2	Hydriodide of malachite green	0.0481	100	5.02
3	Hydrobromide of crystal violet	0.0505	150	6.40
4	Hydriodide of crystal violet	0.0479	100	6.35
5	Nitrate of antipyrin orange	0.0797	100	4.70
6	10-methyl-9-phenyl-acridinium iodide	0.0900	100	6.10
"	"	0.0912	100	6.10

3. Determination of pK of Certain Salts in Aqueous Acetone

A weighed sample of the substance is dissolved in 70 ml of 60% aqueous acetone. If a salt is taken, we add 0.5 equivalents of NaOH, but if a base is taken we add 0.5 equivalents of hydrochloric acid. Next day we determined the solution pH at temperature 19 ± 1°C. Findings are shown in Table 6.

Table 6

Preparation No.	Dissolved Salt	Sample	0.1 n solution added (in ml)		pH
			HCl	NaOH	
1	Hydrobromide of malachite green	0.0588	-	0.72	6.05
2	4,4'-tetramethyl-diamino-triphenyl-carbinol	0.1886	2.72	-	6.05
3	Nitrate of antipyrine orange	0.1004	-	0.95	5.50
4	Diantipyryl-phenylcarbinol	0.1231	1.28	-	5.50
5	4,4'-tetramethyl-diamino-diphenyl-carbinol	0.1102	2.04	-	4.70
6	10-methyl-9-phenyl-acridinium iodide	0.1448	-	1.82	8.60
7	10-methyl-9-phenyl-9-oxy-9,10-dihydro-acridine	0.1515	2.64	-	8.60
		0.1517	2.64	-	8.50
		0.1523	2.65	-	8.55

o Part of line seems to be omitted in this table. (Translator.)

4. Adsorption Spectra of Solutions of the Dyes and Their Carbinol Bases in Nitrobenzene

a) 4,4'-tetramethyl-diamino-triphenylcarbinol and the hydriodide salt of malachite green were dissolved in nitrobenzene. We heated the resulting solutions for 2 hours at 80°C on a water bath, cooled them, and on the following day took the adsorption spectra (Table 7).

The applicability of Baer's Law to solutions of malachite green in nitrobenzene has been demonstrated previously {4}.

The concentration of the dye cation in the nitrobenzene solution of 4,4'-tetramethyl-diamino-triphenylcarbinol was $4.0 \cdot 10^{-5}$ g-ion/1.

Table 7

λ mμ	D: Hydriodide of malachite green C - $4.3 \cdot 10^{-5}$ mole/1.	D: 4,4'-tetramethyl-diamino-triphenylcarbinol C = $5.8 \cdot 10^{-5}$ mole/1.
600	0.42	0.40
620	0.85	0.81
630	1.09	1.04
635	1.15	1.09
640	1.06	1.01
650	0.79	0.75

b) We prepared nitrobenzene solutions of 4,4',4"-hexamethyl-triamino-triphenylcarbinol and of the hydriodide of crystal violet in nitrobenzene. The adsorption spectra of the solutions were taken after three weeks' time (Table 8).

The concentration of the dye cation in the nitrobenzene solution of 4,4',4"-hexamethyl-triamino-triphenylcarbinol was $7.8 \cdot 10^{-5}$ g-ions/1.

Table 8

λ mμ	D: Hydriodide of crystal violet C = 5·10^{-5} mole/l.	4,4',4"-hexamethyl-triamino triphenylcarbinol C = 8·10^{-5} mole/l.
550	0.237	0.444
590	0.450	0.670
600	0.497	0.720
605	0.491	0.700
610	0.468	0.658
620	0.381	0.502

CONCLUSIONS

The carbinol compounds of triarylmethane dyes (Ganch's so-called "pseudo-bases") are capable of dissociating, with splitting off of a hydroxyl group and formation of cations of the dye. This dissociation takes place not only in water, but also in other solvents.

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{3} A. I. SHATENSHTEIN. Teoriya Kislot i osnovanii /Theory of Acids and Bases/. GKhI.*

{4} O. F. GINZBURG, V. P. TERUSHKIN. Zh.Obsh. Khim. 23, 1049 (1953).

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* Abbreviation possibly "National Chemical Press".